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Monitoring ambient-temperature aging of a carbon-fiber/epoxy composite prepreg with photoacoustic spectroscopy

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Abstract

Carbon-fiber/epoxy prepreg sheet was aged at room temperature under low humidity for up to 60 days. At various times during the aging, intact prepreg specimens were analyzed by infrared photoacoustic spectroscopy and laminates were made from the prepreg and tested for interlaminar shear strength. Over the 60 days, the spectra showed small but quantitative changes, but the shear strengths decreased by less than their uncertainty. Partial least squares modeling of the spectra allowed both the prepreg age and the shear strength to be determined from the prepreg spectra. The standard errors of cross validation for the partial least squares models were 1.47 days for prepreg age and 1.4 MPa for interlaminar shear strength of the resulting laminates.

Keywords: A. Prepreg; B. Environmental degradation; D. Chemical analysis; Prepreg out-time

1. Introduction

Carbon-fiber/epoxy composites are widely used in structural applications where strength-to-weight ratios are critical, such as in aircraft production. Composite components are only as reliable as the prepreg material from which they are made, but prepreg material is unstable at ambient-temperature. A realistic estimation of the useful remaining life of prepreg is therefore essential for maintaining quality control and structural integrity while minimizing waste and maintaining production efficiency. Prepreg is normally kept frozen to prevent degradation prior to use, but it begins to deteriorate once it is warmed to ambient temperature. Unfortunately, the thermal-exposure history of prepreg cannot be strictly controlled. Lay-up work on the production-floor can take days for complex parts and may be interrupted. Exposure to moisture affects both how quickly thawed prepreg chemically ages and how it performs during cure [1,2]. There is at present no simple, reliable, production-floor test to determine how much a prepreg sheet may have degraded due to temperature and moisture exposure. Standard quality control tests (e.g., tack, drape) do not correlate accurately with prepreg chemical age. What is needed is an analysis method that is applicable to prepreg material with minimal sample preparation, that has a simple protocol, and that ultimately could be moved to the production floor for on-the-spot determinations. We have examined applying infrared photoacoustic spectroscopy to determining the effective age of prepreg material. The attributes of photoacoustic spectroscopy (PAS) would allow the development of a simple, production-floor test based on it.

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The ambient-temperature age or out-time of epoxy prepregs has definite effects on the properties and composition of the prepreg. Both infrared spectroscopy and high-performance liquid chromatography have shown that the concentrations of epoxy groups and curing agent drop with thawed age [1-4]. The concentration of volatiles also drops over time [4,5], which results in a decrease in tack at ambient-temperature [5,6]. Microscopic investigation shows that the prepreg surface roughens and becomes more irregular with age [7]. These compositional and surface changes affect the functionality of the prepreg during layup and cure. As the ambient-temperature age of prepreg rises, prepreg interlaminar permeability increases markedly [8], the curing heat of reaction decreases [2,4,9], and its curing reactivity either decreases [1,3] or shifts to higher temperature [9]. Higher humidity during aging increases these effects [1,2]. Cole et al. [5] found that epoxy resin flow did not change with prepreg age when measured by standard methods, but they found that the resin content of finished laminates increased with age, implying that resin flow was reduced on the physical and time scales relevant to producing laminate panels.

Determinations of the effects of prepreg age on finished laminate panels have been less consistent. Both Scola et al. [3] and Cole et al. [5] found that the short beam strength of laminates decreased with increasing prepreg age. Cole et al. [5] also observed reductions in compressive strength and modulus. Ji et al. [4] observed drops in flexural strength and modulus. On the other hand, Akay [10] reported no significant effect from prepreg age on any of these laminate properties. Neither Cole et al. [5] nor Akay [10] observed age-related effects on tensile properties, but Ji et al. [4] did. The variable success in correlating prepreg age with laminate performance demonstrates that many other factors affect the composite. Cure cycle properties, such as pressure magnitude and its duration, and hold temperature and its duration all affect the resulting composite [11]. These other factors, however, cannot correct for degraded prepreg.

In the studies cited above, infrared spectroscopy provided a reliable measure of epoxy prepreg age [2-4]. The analysis, however, invariably involved dissolving the resin and drying the solution on an infrared-transmitting crystal. Most typically, the analysis was done by transmission spectroscopy with the solution dried on a salt plate [2-4]. Cole et al. [2] also successfully used attenuated total reflectance, and they tried diffuse reflectance but found it lacked reproducibility. Such methods may reliably measure prepreg degradation, but they are too complex for routine use. Unlike these other spectroscopic sampling methods, PAS can analyze the intact prepreg, allowing virtually all sample preparation to be skipped. PAS is not impeded by the opacity or low reflectivity of the prepreg sheet. PAS works by directly sensing the infrared energy absorbed in a sample, rather than measuring the transmitted or reflected energy [12-14]. In laboratory PAS, the sample typically is sealed in a chamber having a window in one wall and containing a microphone. Intensity-modulated infrared radiation shines on the sample through the window. If the sample absorbs the radiation, its temperature oscillates. The heat deposited within roughly one thermal diffusion length, L , of the sample surface diffuses to the surface and warms the gas surrounding the sample. This causes the temperature and pressure of the gas to oscillate, which the microphone detects as sound waves at the same frequency as the infrared modulation. The bigger the absorption coefficient of the sample is, the larger the heat deposited within a distance L of the surface, and so the stronger the photoacoustic signal is. The photoacoustic signal is therefore proportional to the absorption coefficient. L is approximately the PAS probe depth, and L depends on the modulation frequency, so the user can adjust the probe depth and acquire analytically useful spectra from even highly absorbing materials like carbon-fiber prepregs. For on-site use and analysis of large, intact objects, PAS can be done

with an open-ended chamber that is pressed on or clamped to the object to be tested to create the necessary acoustic seal.

In this work, we have acquired mid-infrared photoacoustic spectra of a series of carbon fiber/epoxy prepreg samples that had been aged at room temperature under low humidity for periods of up to 60 days. Twelve-ply panels were created from the aged prepreg material and tested for short beam strength. The photoacoustic spectra were then correlated with both the thawed aging time and the measured strengths.

2. Experimental procedure

2.1 Materials and specimen preparation

A fresh roll of Toray T700S-12K-50C/#2510 Plain Weave Fabric Prepreg composed of carbon-fiber and epoxy resin was used for the study. Samples cut from the roll were aged from 2 to 60 days at ambient-temperature in zip-lock bags, which contained desiccant to maintain low, constant relative humidity, and then refrozen at the National Institute for Aviation Research (NIAR), Wichita State University. Portions of the controlled-aged prepreps were sent to Iowa State University so that they could be spectroscopically analyzed. The remaining prepreg was made into interlaminar shear strength (ILSS, or short beam strength) test panels at NIAR. Each panel created for the ILSS test was fabricated using 12 plies of prepreg, all oriented in the warp direction, in accordance with Toray material specification number TCSPF-T-FC06 Rev. C. After layup, the panels were vacuum-bagged and held under vacuum overnight and then cured in the morning. The material was cured in a forced-air convection oven equipped with vacuum ports in accordance with the material specification and the following cure cycle:

- (a) A vacuum of 0.745 MPa (22 in. Hg) minimum was applied to the vacuum-bag assembly, which was checked for leaks before beginning the cure cycle. The leak rate was less than 0.068 MPa (2.0 in. Hg) over 5 minutes.
- (b) A temperature ramp from ambient to 132.2 ± 5.6 °C (270 ± 10 °F) at a rate of 1.67 ± 0.56 °C (3.0 ± 1.0 °F) per minute was applied.
- (c) A cure temperature of 132.2 ± 5.6 °C (270 ± 10 °F) was maintained for 120–150 min.
- (d) The temperature was cooled down to 76.7 °C (170 °F) or lower at a rate of 2.5 ± 0.28 °C (4.5 ± 0.5 °F) per minute before removing the vacuum.

When completed, the panels were sent for ultrasonic c-scan before they were cut and tested. The average cured-laminate thickness was 2.64 mm (0.104 in.) in accordance with TCSPF-T-FC06 Rev. C.

2.2 Testing procedure

A PAC 300 detector from MTEC Photoacoustics mounted in a Digilab FTS 7000 FTIR spectrometer was used for the spectroscopic analysis. The sample chamber in the detector has a 1 cm interior diameter and a window at the top through which the infrared beam from the spectrometer enters. Prepreg specimens 9 mm in diameter were cut from the prepreg sheets to fit in the detector. Each specimen was placed face up in the detector with a metal ring atop it to keep the specimen flat and hide its edge, thus assuring that only the face of the specimen was

exposed to the infrared beam and analyzed. The detector was purged with helium immediately prior to spectrum acquisition to minimize interference from water vapor and carbon dioxide, which have strong mid-infrared absorption spectra. In addition a small amount of magnesium perchlorate desiccant was placed in a cup beneath the sample to eliminate any water vapor that might evolve from the sample when it was warmed by the infrared beam during the analysis. This sample handling is typical for FTIR-PAS of solid specimens and is described in more detail elsewhere [15]. Spectra were taken at 8 cm^{-1} resolution and 2.5 kHz scanning speed (0.158 cm/s retardation speed), and 256 scans were co-added.

The spectra were separately correlated with both sample age and interlaminar shear strength by partial least squares (PLS) [16,17] using commercial software (Thermo Galactic GRAMS/AI PLSplus IQ Version 5.1). In PLS, a training set of spectra is acquired from a group of samples whose relevant properties (e.g., out-time age, laminate ILSS) are known and span the range of interest. PLS modeling determines a small set of basis-vector spectra, called factors, by which it can describe all of the training-set spectra. Each training-set spectrum is just a weighted sum of the factors. The factors with the smallest weightings consist mostly of noise and are dropped from the model. PLS then performs a multiple linear regression correlating the factor weightings with the known values of the property being predicted. Once the PLS model is built, the correlated property can be determined for unknown samples directly from the model, as long as the properties of the unknowns fall within the range of those covered by the original training set. Each unknown spectrum is decomposed into the set of factors to determine their weightings. The property value is then predicted from the linear regression equation for the weightings. Many causes of imperfections in spectra (e.g., light scattering, peak saturation) are well known, and various standard “preprocessing” treatments have been developed to correct spectra prior to PLS modeling. In the models discussed here, the spectra were preprocessed by performing multiplicative scatter correction [18] and taking the second derivative of the spectra. Multiplicative scatter correction (MSC) corrects for effects arising from light scattering within the sample, and the second-derivative removes interferences associated with raised and sloped baselines, which these spectra often had because of the infrared absorption by the carbon fibers. Three specimens were prepared for each of the 22 sample ages examined. The spectrum from one of the specimens was used in the training set for building the PLS models. The spectra of the other two specimens were analyzed as unknowns with the completed models to assess their accuracy. In addition, model accuracy was assessed using single-elimination cross-validation. In such cross validations, one member of the training set is removed, and a model is built from the remaining members. The removed spectrum is then analyzed as an unknown. The removed spectrum is returned to the training set, and then a different one is removed and the process is repeated. This is done until all training set members have been removed and analyzed as unknowns. The standard error of cross-validation (SECV) is a measure of model accuracy. It is the root-mean-square difference between the values of the predicted property determined during the cross-validation and their known values.

Although photoacoustic spectroscopy acquires a spectrum from just the top few micrometers to tens of micrometers of a sample, the strong absorption at all wavenumbers by the carbon-fiber fabric in the prepreg produces a strong background, which may be sloped or gently curved. This background does not interfere with the PLS correlations because of the second-derivative preprocessing, but it has been removed from the spectra shown in Figs. 1 and 2 for clarity. In addition, the spectra in the figures are the averages of the three spectra taken at each sample age.

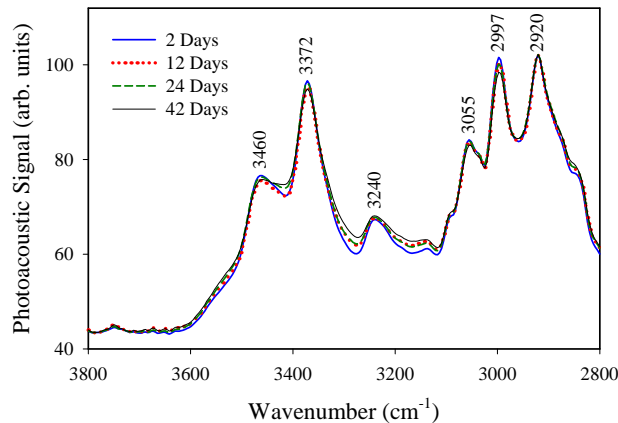


Fig. 1. High-wavenumber region of the mid-infrared photoacoustic spectra of carbon-fiber/epoxy prepregs after aging at ambient temperature for the four indicated periods. Spectra have been scaled to the 2920 cm^{-1} peak.

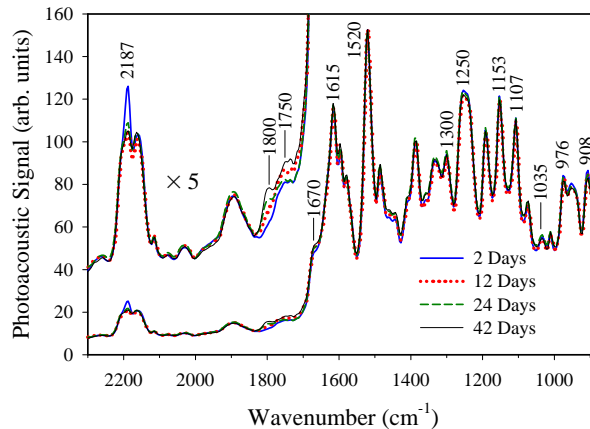


Fig. 2. Low-wavenumber region of the mid-infrared photoacoustic spectra of carbon-fiber/epoxy prepregs after aging at ambient temperature for the four indicated periods. Spectra have been scaled to the 1520 cm^{-1} peak.

Ultrasonic nondestructive testing (NDT) was performed on every ILSS panel prior to machining. A through-transmission (TT) method with 5 MHz transducers was employed using water columns as coupling medium. The NDT instrument (Staveley Workstation with Sonic 200 module) was connected to a custom-built automated nondestructive inspection system to produce ultrasonic c-scan images. The same gain/amplification was used for all the panels so any variation in the c-scan image gray scale is an indication of variation in void content.

ILSS was determined in accordance with ASTM D 2344-00 [19]. The average laminate thickness was 2.64 mm (0.104 inch). Specimen length and width were equal to six and two times the average laminate thickness, respectively. The specimen width and length dimensions were cut on a milling machine equipped with a 180-grit diamond abrasive blade at a cutting speed of 200 m/min. The width dimension was subsequently precision ground on a surface grinding machine. The tests were performed on a 25 kN (5.5 kip) MTS servo-hydraulic load unit equipped with a 2.5 kN (550 lbf) load cell and standard ASTM D2344 test fixture manufactured by Wyoming Test Fixtures, Inc. The tests were performed under room temperature ambient conditions at a loading rate of 1.0 mm (0.04 inch)/min. Eight separate ILSS determinations were made at each sample age tested. These eight measurements were combined into an average ILSS value for each age.

3. Results and discussion

Figs. 1 and 2 show FTIR-PAS spectra of the prepreg at four different ambient-temperature ages. The composition of the prepreg resin studied here is not publicly known, but our spectra closely resemble those of Narmco 5208 reported by Cole et al. [2] and Cizmecioglu et al. [20]. Narmco 5208 consists primarily of tetraglycidyl 4,4'-diaminodiphenylmethane (TGDDM) epoxy resin and diaminodiphenyl sulfone (DDS) curing agent, with a smaller amount of the polyglycidyl ether of bisphenol A novolac epoxy resin [2,20-22]. The peaks in Figs. 1 and 2 at 3055, 2997, 2920, 1615, 1520, 1250, 976, 953, 908 cm^{-1} have been assigned to TGDDM, and the peaks at 3460, 3372, 3240, 1300, 1153, 1107, and 1072 cm^{-1} arise from DDS [2,20]. The small peak at 1035 cm^{-1} comes from the novolac resin [20]. The relative heights of the peaks in

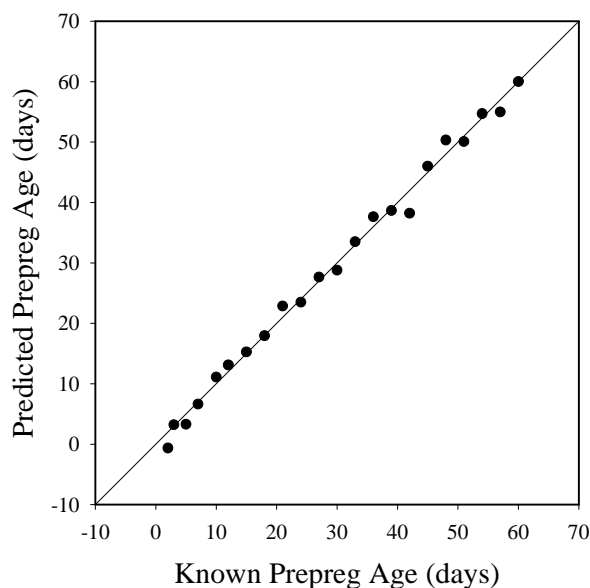


Fig. 3. Cross-validation of the 22-member training set of the PLS model correlating spectra with prepreg age. The diagonal line is the ideal (i.e., predicted = actual).

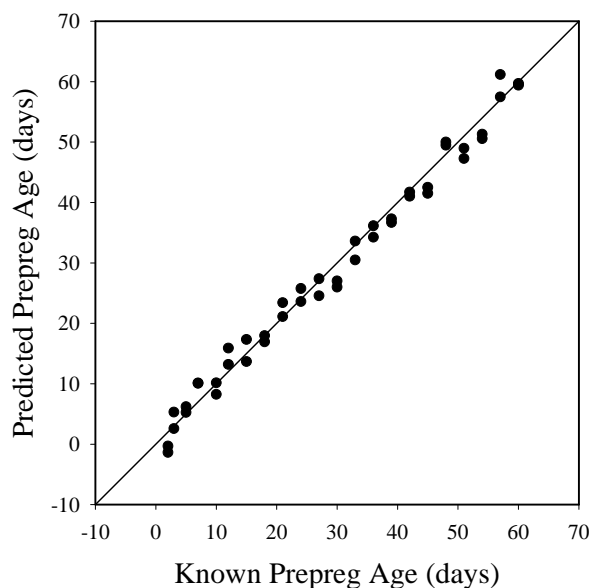


Fig. 4. Analysis of 44 unknowns for prepreg age from the PLS model correlating spectra and age. The diagonal line is the ideal (i.e., predicted = actual).

Figs. 1 and 2 imply that the present resin contains less DDS or its analogue than Narmco 5208 does.

The age-related changes in the spectra are relatively small. The high-wavenumber region in Fig. 1 is dominated by bands arising from aliphatic C–H bonds (3055 , 2997 , and 2920 cm^{-1}) of TGDDM or a similar resin and N–H bonds (3372 cm^{-1}) of DDS or a similar curing agent [2,20]. Aging results in a filling in of the valleys between the 3460 and 3372 cm^{-1} peaks and between the 3372 cm^{-1} peak and 3100 cm^{-1} . It also causes the slight shoulder near 3540 cm^{-1} to increase. These changes may be caused by an increase in hydroxyl concentration because O–H bonds give rise to broad absorptions throughout this region [23]. In addition, the 2997 cm^{-1} band weakens slightly. Fig. 2 shows the low-wavenumber region of the spectra. The bands at 2160 and 2187 cm^{-1} do not appear in the Cole et al. and Cizmecioglu et al. spectra [2,20], indicating that the prepreg resin contains additional functionalities not present in Narmco 5208. Nitrile and cyanate species have peaks in this region [23]. The 2187 cm^{-1} peak clearly decreases in size during the first few days of aging, but it stabilizes after 10–14 days. Two weak bands at 1750 and 1800 cm^{-1} and the shoulder at 1670 cm^{-1} grow with age. Carbonyl (C=O bond) peaks appear in this region [23], and these are often indicators of oxidation. The observed changes are generally not similar to those expected to occur during the cure of an epoxy. Others have used the decrease in the epoxide peaks at 976 , 953 and 908 cm^{-1} as a measure of resin advancement [2,4], but we observe little or no change in them.

Despite the small observed changes in the spectra, PLS successfully modeled the correlation between the FTIR-PAS spectra and prepreg age. Fig. 3 shows the cross-validation results for the model having the smallest SECV. The plot is of the known prepreg age against the age predicted by the PLS model for each of the 22 training set members during the cross-validation. The diagonal line is the ideal (i.e., predicted = actual). The SECV is 1.47 days and r^2

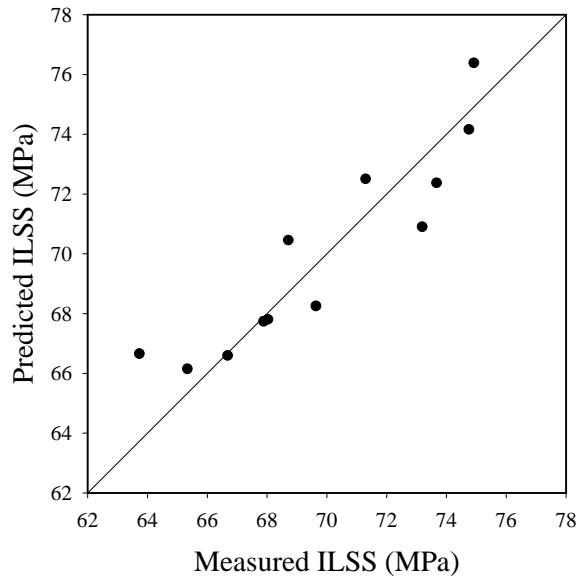


Fig. 5. Cross-validation of the PLS model correlating spectra with interlaminar shear strength. The diagonal line is the ideal (i.e., predicted = actual).

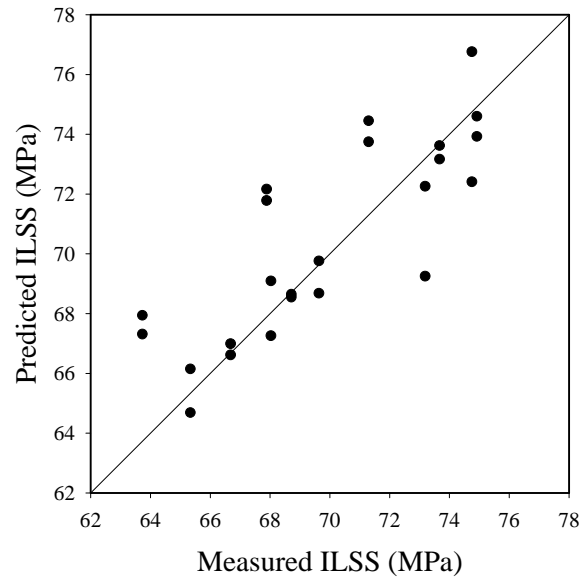


Fig. 6. Analysis of 24 unknowns for interlaminar shear strength from the PLS correlation. The diagonal line is the ideal (i.e., predicted = actual).

is 0.99. The SECV is less than the average spacing between successive data points (2.76 days), which is a very good result. The model uses MSC and second-derivative (21 point Savitsky-Golay) preprocessing, uses only the 3549 to 2851 and 2249 to 1292 cm^{-1} spectrum regions, and has eight factors. Spectra of the 44 specimens used as unknowns were analyzed with the completed PLS model, and Fig. 4 shows the results. The root-mean-square error for the analyses of the unknowns is 2.19 days and r^2 is 0.95.

During the ILSS panel layout process, it was found that the prepreg had become stiffer and lost some of its tackiness after the 33rd day. Average ILSS values were determined for 12 sample ages. PLS modeling successfully correlated the spectra with the average ILSS values. The most accurate PLS model found uses MSC preprocessing and the full 4000 to 397 cm^{-1} range of the spectra with four factors. Fig. 5 shows its cross-validation results. SECV is 1.4 MPa (0.21 ksi) and r^2 is 0.84. Fig. 6 shows the analysis of the spectra of 24 unknowns using the same PLS model, and the root-mean-square error for ILSS of the unknowns is 2.2 MPa (0.31 ksi) and r^2 is 0.82. There is substantially more scatter in the ILSS plots than in the prepreg-age plots. ILSS measurements tend to exhibit scatter with coefficients of variation of a few percent [4,5,24]. The average ILSS value obtained using the ASTM method was 70.4 MPa for the unknowns, so the 2.2 MPa root-mean-square error of the PLS predictions is 3% of that average. The imprecision of the ILSS measurements can account for the scatter observed in Figs. 5 and 6.

The ultrasonic c-scans of the ILSS panels are shown in Fig. 7. The small black dots near the upper one-fifth of the panels are caused by water splash and should not be confused with the panel quality. The large black dots (one on each panel) are 1.27 cm (0.5 inch) diameter foam standards that were adhesively placed onto the panels prior to inspection to show the relative size. Since the equipment settings remained constant for all the panels, changes in c-scan gray shades are indications of changes in panel void content; darker shades mean higher void content. The average grayscale values for the c-scans images in Fig. 7 are given in Table 1. The average

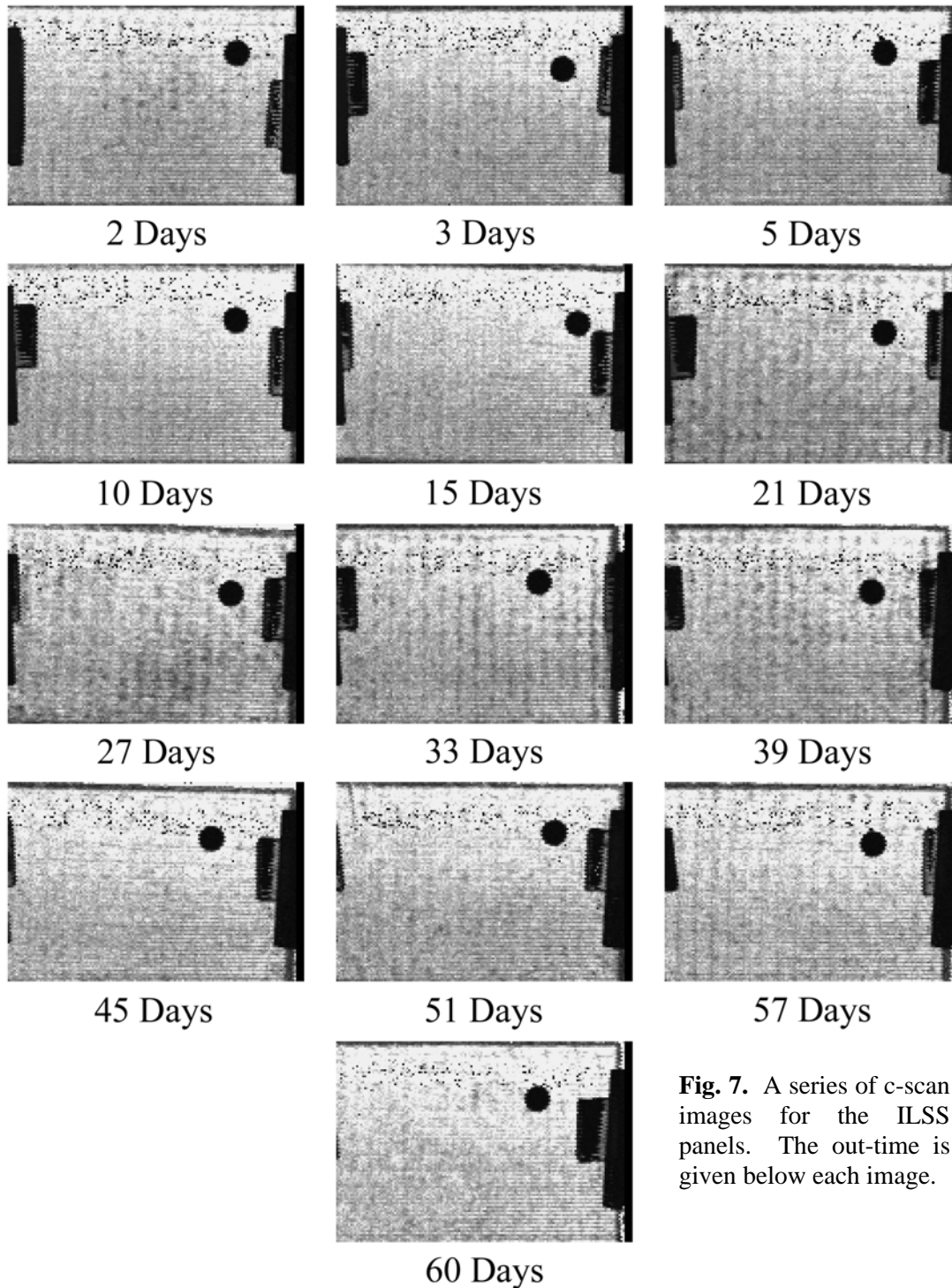


Fig. 7. A series of c-scan images for the ILSS panels. The out-time is given below each image.

grayscale values show a gradual decrease in void content with increasing prepreg out-time, a well known trend with vacuum-bag-only cured materials. The decrease in void content is due to the loss of prepreg tackiness; less tacky prepreps are less able to trap air during layup and allow the air to be drawn out when vacuum is applied, resulting in lower-void-content laminates.

However, lower void content does not necessarily translate into higher ILSS, as will be shown in Fig. 8.

Table 1. Average grayscale value of C-scan images

Prepreg age (days)	Average grayscale value of C-scan image
2	36.8
3	33.8
5	35.6
10	34.5
15	39.8
21	33.0
27	37.1
33	31.1
39	32.6
45	33.8
51	36.8
57	33.8
60	34.9

Fig. 8 shows the ILSS measured as a function of out-time. Eight measurements were made at each out-time and averaged. The figure shows that prepreg out-time does not have a significant impact on ILSS. This also means that ILSS is not a good test method to predict prepreg out-time.

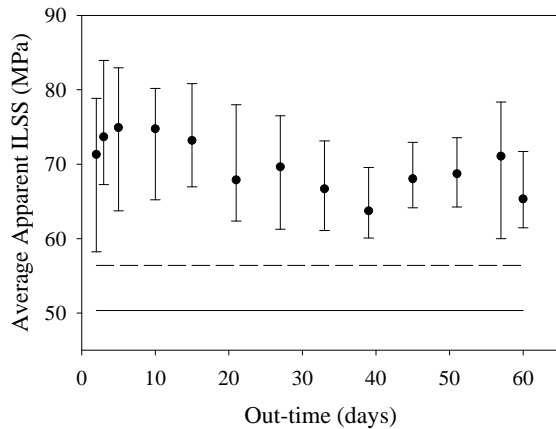


Fig. 8. ILSS as a function of out-time. The error bars indicate the full range of measured values at each out-time. The horizontal lines are the minimum allowed ILSS measurements specified by the manufacturer (dashed) for an average of five measurements and (solid) for individual measurements, as described in the text.

ILSS did not correspond well with void content, as shown by the average grayscale values of the Fig. 7 c-scans given in Table 1. This could be due to the shape and distribution of the voids within the laminate, which cannot be accurately measured with c-scan. In general, the resin in aged prepreg flows less when heated, so the voids tend to be concentrated between the plies, creating the weakest link for interlaminar shear failure. On the other hand, the resin in fresh prepreg tends to flow more when heated, so the voids are more evenly distributed throughout the laminate. The horizontal lines in Fig. 8 are the material specification limits derived from the original material qualification program. Material specification limits are also known as quality control limits or material acceptance limits; they are thresholds that the quality control test results must meet or exceed before the material can be certified to the material specification. Specifically, the dashed horizontal line is the

material specification limit for an average of five ILSS specimens and the solid horizontal line is the material specification limit for the minimum individual of five ILSS specimens. The horizontal lines are shown in Fig. 8 to demonstrate that the entire ILSS test, up to 60 days of prepreg out-time, would have passed the specification limits. However, it is worth noting here that a total of eight specimens were tested for each out-time exposure in this investigation, while the specification limits were designed for five specimens.

4. Conclusion

Infrared PAS spectra of intact prepreg specimens that had been aged at room temperature under desiccation for periods ranging from 2 to 60 days showed only small changes with age, but these changes were reproducible and quantitative. An accurate PLS correlation between the spectra and prepreg age was derived. A PLS correlation between the spectra and ILSS measurements of laminates made from the aged prepreps was also derived. The correlation with ILSS is less precise than the one with age, but consistent with the level of precision of the mechanical measurement. PAS of intact prepreg appears to be well suited to determining the length of exposure of the prepreg to room temperature.

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